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Assembly of Noncentrosymmetric Coordination Polymers by the Integration of Acentric Ba(II)/Sr(II) and Li(I) Coordination Polyhedra

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Presented is a new feasible strategy to construct heterometallic coordination polymers with noncentrosymmetric structure, that is, the integration of acentric [MO_xN_y] (M = Ba, Sr; x + y = 8–10) polyhedron and [LiO_xN_{4-x}] tetrahedron via bridging organic ligands.

Noncentrosymmetric (NCS) materials are of persistent interest due to their applications in photonic areas such as nonlinear optics (NLO) and ferroelectric technologies.¹ In addition to the ongoing efforts to design inorganic NCS compounds, the construction of NCS coordination polymers (CPs) has become a focus in recent years.² Compared to inorganic materials, the modular nature of CPs enables the design at molecular level, which allows for the flexible selection of metal ions and organic ligands from the concern of optimizing functionality.^{2e, 2f}

A straightforward strategy to obtain NCS CPs is the utilization of chiral ligand which may transfer chiral information to the whole structure.^{2b, 2d, 3} Another typical strategy to obtain NCS CPs is the usage of dipolar chromophores pioneered by Lin et al.^{2a, 2e-g} Thus far, the efforts to construct NCS CPs are mainly focused on the design of organic linkers, and most of the known NCS CPs are based on single metal ion, while the creation of heterometallic NCS CPs highlighting the role of metal ions is much less explored.^{2d, 2i, 4} It is noteworthy that recently Du et al. found that the incorporation of alkaline earth metals in cadmium-carboxylate networks could yield heterometallic NCS CPs with a high chance.^{2d, 2i, 4a-c} In fact, in the design of inorganic NCS materials, a common strategy is suggested to involve distinct acentric building units in one crystal structure.⁵ For example, the collaboration of d⁰ transition-metal ions (e.g. Nb⁵⁺, Mo⁶⁺, W⁶⁺) and p-block cations (e.g. Te⁴⁺, I⁵⁺) with stereo-active lone-pair electrons has resulted in Na₂Te₃Mo₃O₁₆,^{5b} BaTeM₂O₉ (M = W, Mo)^{5c} and BaNbO(IO₃)₅^{5e} with large UV SHG responses. While compounds Ln₄GaSbS₉^{5g} and Ln₄InSbS₉^{5h} integrating metal ions with rigid tetrahedral geometry (e.g. Ga³⁺, In³⁺) and lone-pair-

electron-containing Sb³⁺ ion exhibit strong NLO responses in middle IR.

Inspired by the above mentioned achievements, we anticipate developing a new strategy for constructing NCS CPs, that is, to integrate acentric Ba(II)/Sr(II) and Li(I) coordination polyhedra in one structure by bridging organic ligand. The Li(I) ion has the smallest ionic radius and favours acentric four or five coordination modes; while the Ba(II)/Sr(II) ion with a very large ionic radius normally binds to more ligands in a noncentrosymmetric way.⁶ Along this line of consideration, we present here a series of main-group heterometallic NCS CPs prepared by the solvothermal reactions of Ba(II)/Sr(II), Li(I) and carboxylic ligands in *N,N*-dimethylformamide (DMF), namely MLi₂(3,5-PDCH)₂(DMF)₂ (M = Ba in (1), Sr in (2)) and [Ba₃Li₆(3,5-PDCH)₆(DMF)₂]₂·2DMF (3) (3,5-PDCH₃ = pyrazole-3,5-dicarboxylic acid), which represent the first examples of 3D heterometallic CPs simultaneously containing Ba(II)/Sr(II) and Li(I).⁷ The SHG responses of 1-3 are about 2, 2, and 0.5 times that of KDP (KH₂PO₄), respectively.

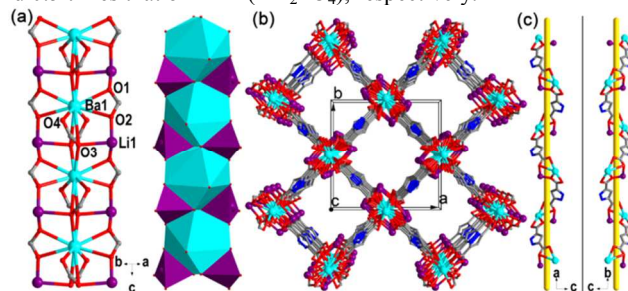


Fig. 1 Structural diagrams of **1** showing (a) the heterometallic [BaLi₂(COO)₄]_n ribbon and polyhedral view of linking modes of Ba²⁺ and Li⁺ coordination polyhedra in the ribbon along the *c* axis, (b) the 3D structure viewed along the *c* axis, and (c) the 2₁ helical chains along the *a* and *b* axes. All the H atoms and DMF molecules are omitted for clarity.

Single-crystal X-ray diffraction analyses reveal that compounds **1** and **2** are isostructural to each other. Thus the structure of **1** as a representative is described, Fig. 1. **1** belongs

to the $P-42_1c$ space group and features a three-dimensional (3D) infinite framework. The crystallographic asymmetric unit contains one formula unit. The Ba^{2+} ion located at the special position with $\bar{4}$ symmetry is deca-coordinated to form a $[BaO_{10}]$ trigonal hexadecahedron. Whereas the Li^+ ion adopts a tetrahedral coordination geometry including a terminal coordinated DMF molecule, Fig. S3a. Apparently the coordination polyhedra of Ba^{2+} or Li^+ ions lack the inversion center. The 3,5-PDCH $^{2-}$ ligand adopts a $(k^1-k^2-\mu_3)-(k^2-k^2-\mu_3)-\mu_6$ coordination mode, Fig. S3b.

Along the c axis, an infinite heterometallic $[BaLi_2(COO)_4]_n$ ribbon is evident which is constructed by the integration of edge-shared $[BaO_{10}]$ polyhedra and $[LiO_4]$ tetrahedra, Fig. 1a. Then each ribbon is interlinked to adjacent four ribbons by 3,5-PDCH $^{2-}$ ligands in $[110]$ and $[1-10]$ directions into a 3D framework with coordinated DMF molecules located in the tunnels along the c axis, Fig. 1b, S4. There exist left-handed and right-handed 2_1 helical chains with a pitch of 15.09 Å along the a and b axes, respectively (Fig. 1c), in which the Li^+ and Ba^{2+} ions are bridged by 3,5-PDCH $^{2-}$ ligands.

3 belongs to the $P2_12_12$ space group. Its structure features a 3D pillar-layered framework, Fig. 2. Its asymmetric unit contains half of the formula unit. The Ba1 ion is deca-coordinated to form a $[Ba(1)O_9N]$ trigonal hexadecahedron, whereas the Ba2 ion is octa-coordinated into a $[Ba(2)O_6N_2]$ trigonal dodecahedron. The three independent Li^+ ions are tetra-coordinated into $[Li(1)O_3N]$, $[Li(2)O_4]$ and $[Li(3)O_4]$ tetrahedra, respectively, Fig. S5. While the 3,5-PDCH $^{2-}$ ligands adopt three different coordination modes (denoted as L-I, L-II and L-III),

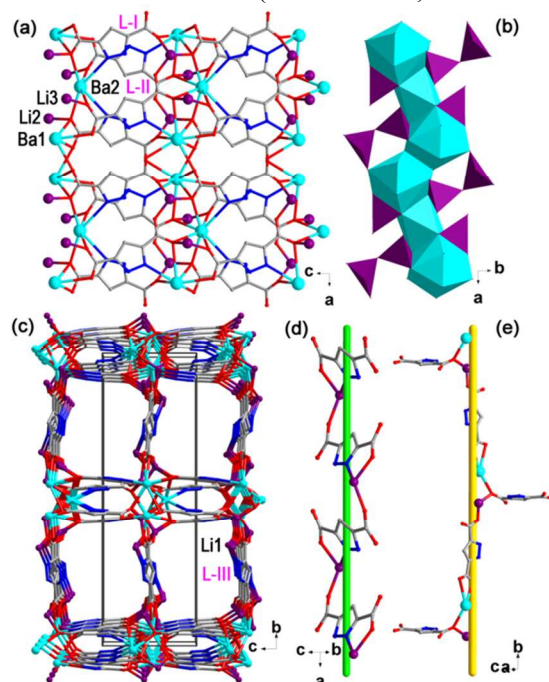


Fig. 2 Structural diagrams of **3** showing (a) the 2D layer waved by L-I and L-II linking Ba(1), Ba(2), Li(2) and Li(3) in the ac plane, (b) the heterometallic ribbon of Ba^{2+} and Li^+ coordination polyhedra, (c) the 3D “pillar-layered” structure viewed along the a axis, and (d) and (e) the helical chains along the a and b axes, respectively. All the H atoms and DMF molecules are omitted for clarity.

Fig. S6. In the ac plane, the L-I and L-II link Ba1, Ba2, Li2 and Li3 into a 2D $[Ba_3Li_4(3,5-PDCH)_4]_n$ layer, Fig. 2a, in which a metal-carboxylate ribbon extending along the a axis is evident, Fig. 2b. Along the b axis, these 2D layers are interlinked by L-III as pillars to form a 3D framework, further, Li1 links L-III into a 2_1 helical chain with a pitch of 10.95 Å running along the a axis, Fig. 2c-d. The uncoordinated DMF molecules are found in the free spaces, whereas all the DMF molecules are oriented towards the tunnels along the a axis, Fig. S8. Another chiral chain also exists, that is, the Li2 and Ba1 are alternatingly linked by L-III and O11 of L-I into a right-handed helical chain with a pitch of 28.59 Å running along the 2_1 -axis parallel to the b axis, Fig. 2e. Detailed structural descriptions are shown in the ESI.

The title compounds represent the first exploration on designing heterometallic NCS CPs simultaneously containing Ba(II)/Sr(II) and Li(I).^{7f} From a structural point of view, the large ionic radius of Ba(II)/Sr(II) ion facilitates it to bind more ligands which usually makes the $[M(O_xN_y)]$ ($M = Ba, Sr$) polyhedron be twisted and aberrant thus noncentrosymmetric.^{6a, 6b} Likewise, the $[LiO_xN_{4-x}]$ tetrahedron, has inherent acentric geometry. In fact, the presence of acentric building units does not ensure the whole structure being NCS, while the interlinking modes of these units play a vital role. In the 0D, 1D or 2D CP compounds, the adjacent acentric clusters/chains/layers tend to be related via an inversion center leading to centrosymmetric (CS) structures.^{2b} There are only nine Ba-Li-based coordination compounds in the CCDC database, in which the organic ligands serve as terminal ligands for metal ions to produce 0D molecules.⁷ Indeed, in these structures the molecules favourite CS rather than NCS packing upon supramolecular interactions therefore only one out of nine compounds adopts a NCS structure.^{7f} By comparison, in

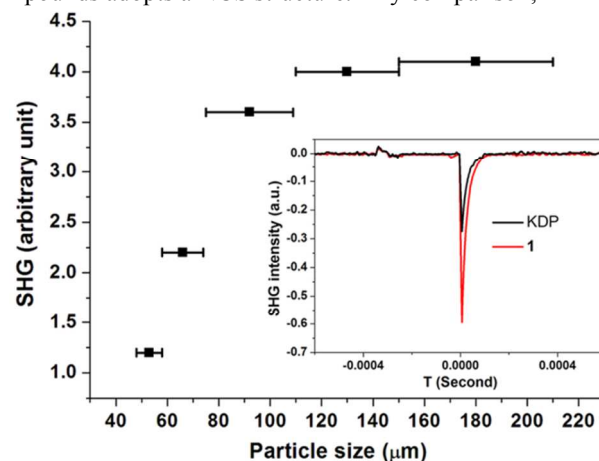


Fig. 3 Particle size dependence of the SHG intensity for **1**. Inset: Oscilloscope traces of the SHG signals of **1** and KDP in the particle size of 150-212 μm.

compounds **1-3** the 3,5-PDCH $^{2-}$ ligands interconnect the Ba(II)/Sr(II) and Li(I) into 3D structures in which the acentric polyhedra of $[M(O_xN_y)]$ ($M = Ba, Sr$) and $[LiO_xN_{4-x}]$ adopt edge-shared or/and corner-shared linking modes like that in the

3D inorganic structures,^{5b, 5e, 5f} thus increasing the chance of forming NCS structures.

Considering the NCS structure, the SHG responses of **1-3** were investigated on the powder samples by using the Kurtz–Perry method.⁸ An approximate estimation was carried out on a pulsed Q-switched Nd:YAG laser at a wavelength of 1064 nm. The intensity of the green light ($\lambda = 532$ nm) produced by the crystal powder of **1-3** is about 2, 2 and 0.5 times that of a KDP marker in the same particle size, respectively. For **1**, the SHG effect increases with particle size and plateaus at a maximum value when the particle size is large enough, revealing phase-matching behaviour, Fig. 3. The second-order susceptibility $\chi^{(2)}_{\text{eff}}$ of a KDP powder sample is about 0.36 pm/V, so the derived second-order susceptibility $\chi^{(2)}_{\text{eff}}$ for **1** is 0.72 pm/V.

The density functional theory (DFT) studies were carried out for both **1** and **2** to study their energy band structures and optical properties. Since **1** and **2** are isostructural to each other, we take **1** as an example to analyse the calculated results. Figure S13 shows the calculated band structures of **1** along high symmetry points in the first Brillouin zone which informs that the region of the highest occupied valence band (HVB) nearby the Fermi level is occupied by O-2p states of 3,5-PDCH²⁻ ligands, of which the charge densities are shown in Fig. 4. This feature illustrates that the 3,5-PDCH²⁻ ligands can make more contributions than coordinated DMF molecules to the SHG performance of **1**. The calculated results reveal that the band gap of **1** is 3.92 eV, which is consistent with the experimental value (4.40 eV), Fig. S16.

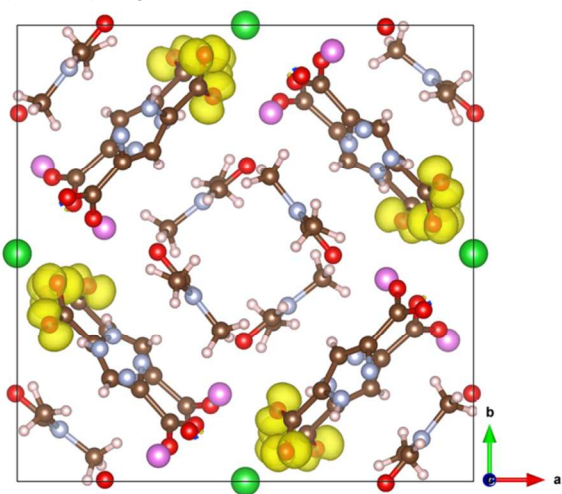


Fig. 4 The calculated charge distributions of the highest occupied valence band near the Fermi level for **1**.

The space group of **1** belongs to class $\bar{4}2m$, so there are three nonvanishing tensors (d_{14} , d_{25} , d_{36}) of second-order susceptibility. In the low-energy region and under the restriction of Kleinman's symmetry, only one independent SHG tensor component d_{36} is considered. The calculated d_{36} at a wavelength of 1064 nm (1.167 eV) is 0.52 pm/V, Fig. S15, which is comparable with our experimentally derived $d^{(2)}_{\text{eff}}$ coefficient for **1** (0.72 pm/V).

In summary, with a new structural constructing strategy, we obtained a new category of NCS CPs containing both Ba(II)/Sr(II) and Li(I). The high chance of obtaining NCS structures may be due to the integration of Li(I) ions with acentric $[\text{LiO}_x\text{N}_{4-x}]$ coordination tetrahedron and Ba(II)/Sr(II) ions with aberrant coordination geometry via the unique linking of asymmetric bridging ligands under solvothermal conditions. The SHG responses of these compounds are moderate and that of compound **1** features phase-matching behaviour. It shall be valuable to further exploit this new strategy to synthesize heterometallic CPs with better SHG performance.

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† Electronic Supplementary Information (ESI) available: Crystallographic data in CIF format; Experimental details, Elemental analyses, X-ray crystallography; more structural details; PXRD patterns; TGA curves; IR spectra; oscilloscope traces of the SHG signals; theoretical calculation results; UV spectra and crystal photographs. CCDC nos. 1036746 (**1**), 1036747 (**2**) and 1036748 (**3**) contain the supplementary crystallographic data for this paper. See DOI: 10.1039/c000000x/.

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